Int. J. Electrochem. Sci., 9 **(2014)** 1557 - 1564

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

PEDOT Nanowires and Platinum Nanoparticles Modified Electrodes to be Assayed in Formic Acid Electro-oxidation

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Received: 2 October 2013 / *Accepted:* 31 October 2013 / *Published:* 5 January 2014

In the current work, the formic acid electro-oxidation process was studied and, to favor the electro-catalysis, platinum nanoparticles dispersion over PEDOT polymeric deposits in the form of nanowires was accomplished. To this end, the previously tested methodology, that allowed direct obtention of polythiophene nanowires on the electrode by purely electrochemical means, is proposed. Here, the EDOT electro-oxidation on Pt|*template*, electrodes allowed obtaining PEDOT nanowires with a diameter of 6.7 nm, suggesting that the method could be extended to the preparation of other conductive polymer nanowires. Therefore, trying to compare and improve the HCOOH electro-oxidation process on PEDOT nanowires, with respect to studies already performed with polythiophene massive deposits or as nanowires, Pt was dispersed utilizing previously proposed approach and found that nanometer-sized PEDOT material obtained with Pt dispersed nanoparticles markedly favor HCOOH electro-oxidation causing a current response increase, as well as a decrease of the acid oxidation potential. Thereby this electrode material represents an important contribution for future applications in the preparation of fuel cells, enabling lower energy consumption and increase of electrical energy production.

Keywords: poly(3,4-ethylenedioxythiophene), PEDOT, nanoparticles, formic acid electro-oxidation, electro-polymerization, electro-catalysis.

1. INTRODUCTION

Energy consumption increases every day and, considering the pollution produced by fossil fuels, global warming and climate change, it becomes increasingly necessary to implement renewable energy sources such as wind, sunlight or hydroelectricity [1]. However, these energy sources depend on the environment and can present constant fluctuations, which makes essential to develop technologies for storage that can maintain the quality of the electrical systems [2]. Currently, different devices for energy storage exist, *e.g.* batteries, supercapacitors and fuel cells, among others [1-3].

This explains the significant efforts being made toward optimizing the performance of these systems designed, primarily, to improve the materials they are constructed from, as these are responsible for the characteristics of each device [3]. It is also essential to reduce production costs of these storage devices. An attractive alternative is the use of fuel cells [4], which are devices that convert the chemical energy of molecules bond breaking into electrical energy in a fairly compact device. A variety of fuel molecules have been used in these cells, *e.g.* H_2 and MeOH. However, when comparing these substances with formic acid (HCOOH) the latter exhibits lower toxicity and lower combustion [5], in addition its transportation and storage is safer as compared to gaseous and liquid hydrogen, which makes it an attractive material for fuel cells development.

The catalyzed formic acid electro-oxidation reaction mechanism is as follows [6]:

$$HCOOH \rightarrow CO_2 + 2H^+ + 2e^- \qquad (1)$$

This is the first direct reaction pathway. Concomitantly, the following occurs:

$$HCOOH \rightarrow CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^- \qquad (2)$$

This second reaction is known as the indirect pathway that poisons the anode owing to carbon monoxide adsorption onto the electrode surface [7], decreasing the overall device performance. This whole process is known as the dual pathway process. Therefore, electrode material choice is an important issue to be taken into account. Consequently, HCOOH electro-oxidation has been conducted on different anode materials, for instance, in recent studies electrode modification with a conductive polymer, on which nanoparticles of Pt and/or Pd can also be dispersed, has been implemented. This revealed that an increase in the electro-catalytic activity of HCOOH oxidation takes place [8,9].

Considering that conducting polymers applications have been favored by using them as nanostructure, our research group obtained polythiophene (Pth) nanowires, with a diameter of 5.7 nm, using for the first time only electrochemical techniques [10]. To this purpose, Pt electrodes were modified with a silica *template*, also obtained by electrochemical means and, upon the Pth nanofibers, Pt nanoparticles were incorporated. The modified electrodes were tested in the electro-oxidation of formic acid, affording more favorable results as compared to those obtained by carrying out the same process upon the massive polymer [9]. Such electrodes could be used as anode in fuel cells.

It has also been suggested that the thickness of the polymer film where the inclusion of metal micro/nano-particles (Pt or Pd) occurs determines the yield of the electro-oxidation process, being higher for thinner polymer films, since a thickness increase provokes a charge-transfer resistance rise. Therefore, it was demonstrated that conductive polymer nanostructures are also materials with potential applications in electro-catalysis. With the aim of improving the obtained results, the electro-oxidation of formic acid using the polymer poly(3,4-ethylenedioxythiophene), PEDOT, will be studied. This polymer belongs to the alkylenedioxythiophene family, that possesses alkylene dioxy moities in position 3- and 4- of the heterocycle, generating thus a polymer with improved properties with respect to the starting material (Pth or polypyrrole) by lowering the oxidation potential of the monomer and decreasing the electronic *band gap* of the π system, conferring it greater stability in its oxidized state, high conductivity, etc. [11,12], becoming thus one of the most interesting conductive polymers in recent years. Its properties have enabled using it in various applications, aimed at producing supercapacitors, transparent materials and electron acceptors, OLEDs, solar cells [13], electrochromic devices, electrochemical sensors [14] and also in formic acid electro-oxidation. [15]. Moreover, alike to other polymers, PEDOT applications have been improved to be obtained as nanostructures, *e.g.* nano-tubes [16-18], nano-fibers [19] and recently, nano-wires [20-24].

Regarding these facts and that the obtained nanostructured material presents a larger effective area, the electrochemical behavior will be verified studying the formic acid electro-oxidation process and, to favor electro-catalysis, dispersion of platinum nanoparticles over these polymeric deposits will be accomplished attempting to compare and improve the acid electro-oxidation process on PEDOT nanowires, with respect to the studies conducted utilizing massive deposits or polythiophene nanowires [8,9].

2. EXPERIMENTAL

Silica films (*template*) were potentiostatically deposited onto a non-annealed Pt disc electrode (2 mm diameter). Precursor solution was prepared mixing 10 mL of a solution containing $5.0\cdot10^{-2}$ $mol\cdot L^{-1}$ KNO_3 (supporting electrolyte, Merck, p.a.), $5.0\cdot10^{-4}$ $mol\cdot L^{-1}$ HCl (Merck, p.a.) in bidistilled water:ethanol (50:50 v/v) with 1.15 mmol of cetyltrimethylammonium bromide, CTAB (surfactant, Aldrich 95%), 3.40 mmol tetraethyl-orthosilicate, TEOS, (Sigma–Aldrich, 99.999%). Prior to each experiment the solution was stirred for 2.5 h. Electrochemical methods and characterization of the formed silica film have been reported elsewhere [25]. Permeability estimation of the mesoporous silica modified electrodes was accomplished employing a $1.24\cdot10^{-3}$ $mol\cdot L^{-1}$ ferrocene (redox probe, Aldrich, 98%) solution and $1.0\cdot10^{-1}$ $mol\cdot L^{-1}$ tetrabutylammonium hexafluorophosphate, $TBAPF_6$, (Aldrich, 98%), as supporting electrolyte, in anhydrous HPLC grade CH_3CN (Aldrich).

A silica modified Pt electrode was used as working electrode for PEDOT potentiostatic electro-polymerization. A Pt|nano-wire-PEDOT modified electrode (Pt|nw-PEDOT) was obtained as reported elsewhere [10]. Unless otherwise stated, all potentials quoted in this paper are referred to an Ag|AgCl electrode in tetramethylammonium chloride to match the potential of a saturated calomel electrode (SCE) at room temperature (20 ºC) [26]. A Pt gauze of large geometrical area separated from the cell main compartment by a fine glass sinter was used as counter electrode. $1\cdot10^{-2}$ $mol\cdot L^{-1}$ ethylenedioxythiophene, EDOT (monomer, Aldrich, 99+%) and $1\cdot10^{-1}$ $mol\cdot L^{-1}$ $TBAPF_6$ in CH_3CN was employed as working solution. To assess nanowire effect on electrode performance, another modified electrode without silica template was assembled, *i.e.* a conventional platinum PEDOT electrode, Pt|PEDOT. Electrode characterization was conducted by studying its electrochemical behavior in different solutions, one containing ferrocene and the other just supporting electrolyte.

Preparation of platinum|nw-PEDOT/platinum-nano-particles electrodes (Pt|nw-PEDOT/Pt-np) was accomplished as reported elsewhere [8, 9] by cycling the Pt|nw-PEDOT electrode in a $1.0\cdot10^{-3}$ $mol\cdot L^{-1}$ H_2PtCl_6 + $1.0\cdot10^{-1}$ $mol\cdot L^{-1}$ KPF_6 aqueous solution. The dispersion of Pt-np over the polymeric matrix was performed utilizing a platinization cycle (PC) based on the *p-doping* process of the polymer by stepping the potential from 0.1 V for 6 min to – 0.50 V during 10 s. At 0.1 V the polymer is oxidized, generating positive charges within the film and, consequently, incorporating anions ($PtCl_6^{-2}$)

from the solution; this potential step is applied for 6 min in order to guarantee maximum anion incorporation. Then, a short -0.50 V reducing potential step is applied, for 10 s, in order to electro-crystallize the $PtCl_6^{-2}$ from the polymer matrix, producing the corresponding platinum particles dispersion. The PC was also applied to the Pt|PEDOT electrode affording a platinum|PEDOT/platinum nano-particles modified electrode (Pt|PEDOT/Pt-np).

To estimate platinum surface from the modified electrodes, their electrochemical response was measured in a $5.0\cdot10^{-1}$ $mol\cdot L^{-1}$ sulfuric acid solution. Cyclic voltammetry between -0.2 and 1.3 V was used at 0.01 $V\cdot s^{-1}$ until a stable response was attained. These data were used to normalize current density using the Pt surface area estimated from the platinum oxide reduction signal.

The electro-catalytic activity of these electrodes toward formic acid electro-oxidation was determined by cycling them into a $1.0\cdot10^{-1}$ $mol\cdot L^{-1}$ HCOOH + $1.0\cdot10^{-1}$ $mol\cdot L^{-1}$ KPF_6 aqueous solution between -0.20 and 1.00 V at 0.01 $V\cdot s^{-1}$.

All electrochemical experiments were conducted at room temperature on a PALM SENS portable potentiostat.

Transmission electron microscopy (TEM) images were obtained on a JEOL/JEM 1200 EX II microscope at an acceleration voltage of 80 kV. Samples for TEM measurements were prepared by mechanically removing (scraping) some pieces of the deposit, which were directly supported on a nickel grid.

3. RESULTS AND DISCUSSION

Figure 1 shows the silicon oxide *template* formation voltammetric profile, after applying a reduction potential sweep between 0 and -2 V. A current decrease was observed with increasing number of cycles, which is consistent with the electro-deposition processes described for semiconductor materials. Hence, once the potential at which the formation of *template* electrodeposition starts (-0.7 to -1.1 V), the potential and optimal formation time of the *template* was determined by applying potential pulses or steps and, for each obtained electro-deposit, its permeability was evaluated in a ferrocene solution [10, 25].

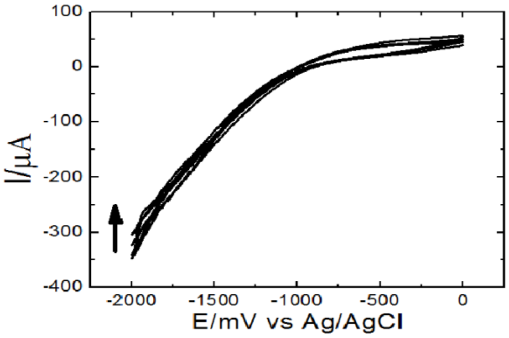

Figure 1. Potentiodynamic profiles recorded during *template* electro-deposition. Interface: Pt $5.0\cdot10^{-2}$ mol L^{-1} KNO_3 + $5.0\cdot10^{-4}$ $mol\cdot L^{-1}$ HCl + 1.15 mmol CTAB + 3.40 mmol TEOS in a bidistilled water-ethanol mixture (50:50 v/v). ν 100 $mV\cdot s^{-1}$.

Figure 2 compares the responses of modified electrode (Pt|*template)* in the same solution that enables determining the optimum conditions for *template* formation, namely applying -0.9 V for 5 s. Under these conditions, a higher current response was observed and a greater probability of molecular permeability to obtain PEDOT nanowires on the modified surface would exist.

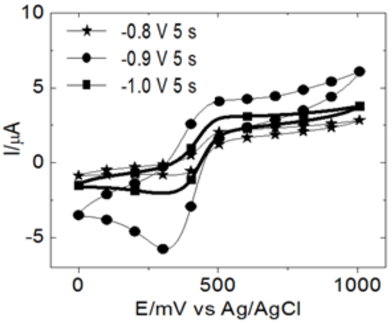

Figure 2. Potentiodynamic profiles recorded fot *templates* obtained under the conditions indicated in the insert.

Subsequently films were formed on the unmodified electrode ("conventional growth: massive PEDOT obtention") and *template* modified electrode ("growth in confined spaces: nanowires obtention) using the Pt|*template* electrode as the working electrode for EDOT polymerization using the potentiostatic technique. Different potentials and electro-polymerization times were applied. Figure 3a shows i/t transients recorded during EDOT electro-polymerization on Pt electrode and Pt|*template* at the optimum potential found in each case for the formation of the conducting polymer deposit. Initial current decrease was attributed to monomer diffusion from the solution to the electrode surface, until, after some time, the nucleation and growth process takes place, which accounts for the current increased [27-29].

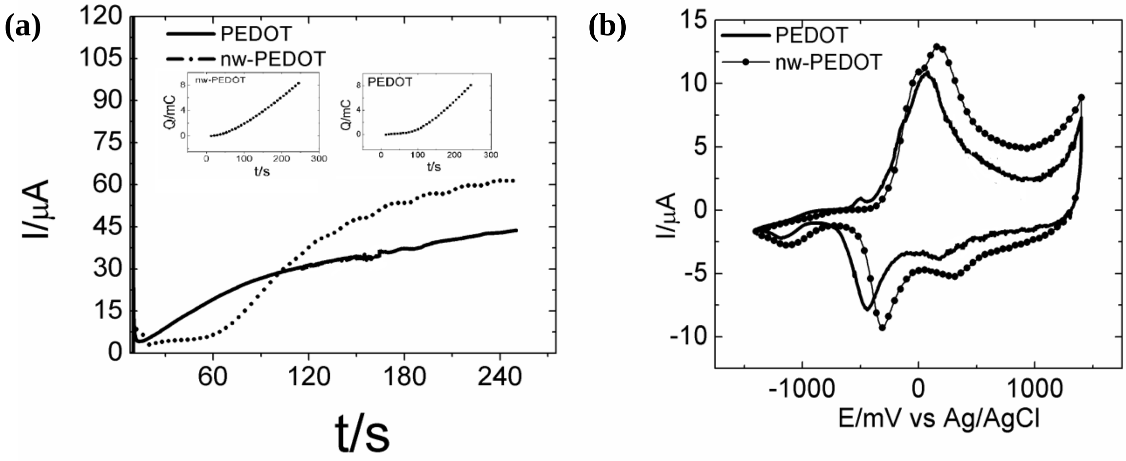

Figure 3. a) i/t transients recorded during PEDOT electropolymerization on massive Pt (PEDOT) and P|t*template* (Pt|nw-PEDOT) from $1{\cdot}10^{-2}$ mol·L^{-1} EDOT + $1{\cdot}10^{-1}$ mol·L^{-1} TBAPF$_6$ in CH$_3$CN; **b)** potentiodynamic response of modified electrodes prepared in (a).

Moreover, the figure inserts show the respective profiles of charge evolution over time, indicating that the polymer obtained on the Pt|*template* electrode accumulates a larger charge (nw-PEDOT 8.5 mC and PEDOT 8.3 mC), for the same area of the supporting electrode. In Fig. 3b the responses of electro-deposits obtained on the two types of electrode in supporting electrolyte solution are compared; it becomes evident the greater current response of the electro-deposit obtained on Pt|*template,* consistent with a larger effective area.

The nw-PEDOT electro-deposits were mechanically removed from the working electrode for TEM analysis. Figure 4 depicts images that corroborate the formation of PEDOT nanowires with a diameter of 6.7 nm. This finding explains the new properties with respect to the conventional polymer film and confirms the achievement of the proposed goal with regard to the obtention of nanostructures of this polymer, as previously done with Pth [10].

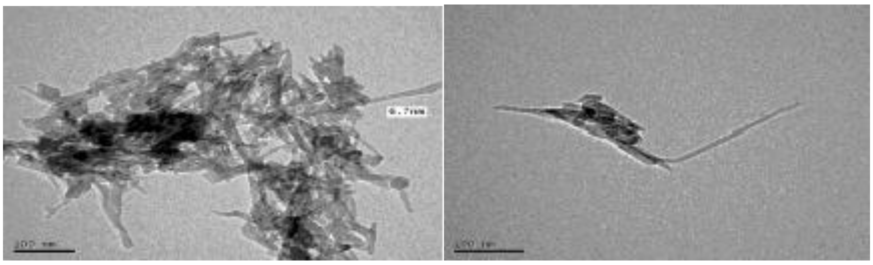

Figure 4. TEM images of nw-PEDOT obtained under Fig. 3 conditions

The effect of platinum nanoparticles dispersion over Pt|PEDOT and Pt|nw-PEDOT electrodes on their electrocatalytic ability, concerning to formic acid electro-oxidation, was then investigated. The method relies on the *p-doping* process of the PEDOT polymer, as described in experimental and explained in similar works previously conducted by our working group [8, 9].

Figure 5a shows voltammograms of HCOOH electro-oxidation at Pt|PEDOT and Pt|nw-PEDOT electrodes. As expected, in none of the two cases appreciable electro-catalytic activity toward HCOOH electro-oxidation was observed on electrodes modified with the polymer alone: the same profile recorded in just supporting electrolyte was obtained.

Figure 5b shows HCOOH electro-oxidation on Pt|PEDOT and Pt|nw-PEDOT polymer modified electrodes after Pt nano-particles dispersion. The Pt|PEDOTPt-np and Pt|nw-PEDOTPt-np electrodes exhibit now a clear electro-catalytic activity for the oxidation of these small molecules [8, 9, 15]. It is noteworthy that an appreciable increase in the electro-catalytic activity on Pt|nw-PEDOTPt-np, as compared with Pt|PEDOTPt-np, was observed. This difference becomes significantly higher when the Pt dispersion was performed employing two PC, as seen in Fig. 5c.

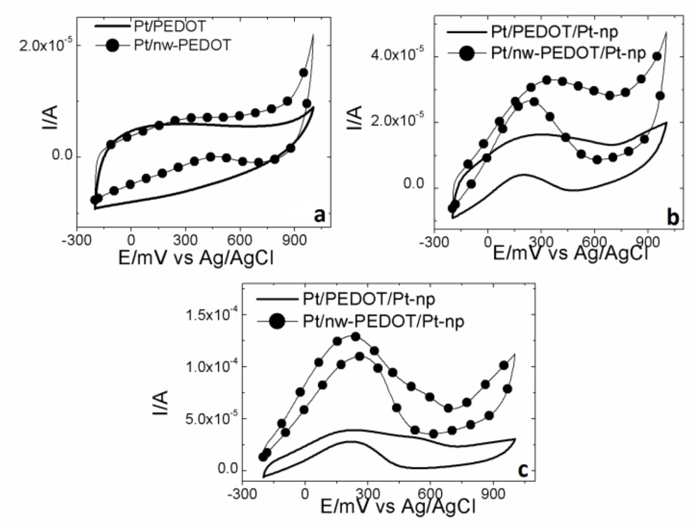

Figure 5. Voltammetric response of HCOOH on: **a)** Pt electrodes coated only with massive or nanostructured PEDOT; **b)** same electrodes as in (a) with dispersed Pt particles using one PC, and **c)** using two PCs.

Figure 5c shows precisely the best recorded response with such modified electrodes, that represents an important contribution with regard to this subject, since, besides the important current increase as compared with similar electrodes of identical geometric surface area, e.g. massive PEDOT, and massive or Pt dispersed nano-structurated Pth [9], here the anodic scan revealed a decrease of the HCOOH electro-oxidation potential on Pt|PEDOTPt-np electrode applying either 1 or 2 PCs (335 mV and 237 mV for one or two cycles, respectively). This decrease of *ca.* 100 mV becomes a significant reduction in the energy consumption of this system, which is much higher when compared with those previously mentioned, namely with polythiophene nano-wires and PEDOT polymer this process occurs, respectively, at 550 and 600 mV [15, 9]. Consequently, the herein assembled system can be set forth as a beneficial candidate for the development of fuel cells.

The reported data also revealed that although Pt was electro-deposited under the same conditions on both PEDOT electrodes, the polymer electro-synthesized as nanowires is responsible for the most significant improvement in the electro-catalytic activity toward HCOOH electro-oxidation.

4. CONCLUSIONS

EDOT electro-oxidation on Pt|*template* electrodes allowed the preparation of PEDOT nano-wires with a diameter of 6.7 nm. This fact leads us to propose that the approach previously used to prepare Pth- and now PEDOT-nano-structures could be extended to the preparation of nanowires of other conducting polymers.

Nanometric dimensions of PEDOT material obtained with Pt dispersed nanoparticles favor the HCOOH electro-oxidation process, bringing about both an increase in current response, as well as a decrease of the acid oxidation potential. Consequently, this electrode material signifies an important contribution for future applications in the preparation of fuel cells, enabling lower energy consumption and to increase the production of electrical energy.

ACKNOWLEDGEMENTS
The authors thank CONICYT financial support through FONDECYT Project 1100055.

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